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Adsorption method for producing hydrogen and device for carrying out said method.

The present invention relates to the methods for producing/purifying hydrogen by Pressure Swing Adsorption in a PSA unit of a feedstock gas at a first pressure containing hydrogen, with compressed waste being sent to a fuel gas mixture distribution network at a second pressure and also containing hydrogen and intended to supply various user stations on the site or nearby.

In conventional installations for the production of from a feedstock gas, the hydrogen produced, give or take pressure drops, at the high 15 pressure of the feedstock gas, the waste from the PSA for its part generally being discharged at low pressure into a fuel gas mixture distribution network (known as the fuel gas network) present on large industrial sites 20 and carrying medium-pressure hydrogen and hydrocarbon mixtures originating from various blowdowns intended to be burnt, particularly in a boiler, produce steam.

These PSA units have the defect of being limited in their extraction efficiency, which means that a not insignificant proportion of the hydrogen from the feedstock gas is lost in the waste and in the fuel gas mixture network.

In order to progress from an efficiency slightly in excess of 72% to an efficiency slightly in excess of 80%, it has been proposed that the equalizings between the cylinders of the PSA unit be proliferated, something which nonetheless entails a great deal of investment (a larger number of adsorbers, which are generally larger individually).

A second approach toward improving the efficiency is to reduce the regeneration pressure by extracting the waste at a reduced pressure slightly higher than atmospheric pressure, it then being possible for the efficiency, at the expense of the addition of a compressor, to reach values of the order of 90%.

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Furthermore, by recirculating, with compression, some of the PSA waste in the feedstock gas, it is possible to achieve efficiencies of the order of 95%, but at the expense of an additional compressor.

It is an object of the present invention to propose an improved method for producing hydrogen that makes it possible, without significant on-cost, to obtain efficiencies in excess of 95%, attaining or even exceeding 100%.

In order to do this, the method according to the invention further comprises the step of tapping off a fraction of the fuel gas mixture from the distribution network, of compressing it more or less to the pressure of the feedstock gas and of injecting it by way of additional feedstock gas into the PSA unit, for example mixed in with the feedstock gas.

The reasoning behind this is as follows: whereas, even with a hydrogen-rich feedstock gas, for example one having a hydrogen content in excess of 70%, composition of the waste rapidly becomes lean when the efficiency of the PSA unit is increased, soon dropping below 30% when the extraction efficiencies exceed 85%, the inventors have demonstrated that, in most cases, hydrogen content in the fuel qas distribution network was above these values, generally of the order of 35 to 50%, and that it was therefore sensible to form a secondary feed to the PSA unit using this hydrogen-rich fluid rather than using recirculated waste.

Using the method according to the invention, for the same production, it will be necessary to introduce less feedstock gas, thus reducing the compression required and generally the size of the PSA unit for a saving in terms of energy and in terms of investment. It also becomes possible, for the same level of impurities introduced into the PSA unit and/or for the same quantity of compressed gas, to process appreciably more hydrogen and increase production in order, as mentioned hereinabove, to achieve efficiencies in excess of 98%.

The use of multiple beds employing different adsorbents with specific functionalities, such as activated alumina, silica gels, activated carbons and appropriate zeolites, allows precise control over the introduction into the PSAs of undesirable components normally not present in the main feedstock gas.

- 20 Another subject of the present invention is an installation for implementing this method, comprising:
 - at least one feedstock gas supply pipe;

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- at least one line of a fuel gas mixture distribution network;
- 25 at least one PSA unit for separating gases by adsorption having one inlet connected to the feedstock gas pipe, a production gas outlet and at least one waste gas outlet;
- a first compressor connecting the waste gas outlet 30 to the fuel gas mixture line; and
 - a second compressor connecting the compressible gas mixture line to the inlet of the PSA unit, typically to the feedstock gas pipe.
- According to a more specific feature of the invention, the first and second compressors use common subassemblies and for example constitute different compression stages on a common drive line.

With such an arrangement, the addition of the secondary feed to the PSA unit which is obtained by compressing a fraction tapped off the fuel gas mixture distribution network makes it possible, for the better by comparison with a conventional solution, to increase the hydrogen extraction efficiency and to do so more effectively than can be achieved by recirculating some of the PSA unit waste.

- The present invention will now be described in conjunction with an embodiment given by way of non-limiting illustration, with reference to the attached drawing in which:
- 15 figure 1 is a schematic view of an installation for implementing the method according to the invention.

The single figure shows a PSA unit for producing hydrogen by pressure swing adsorption 1 comprising at least four adsorbers each containing at least one adsorbent capable of separating hydrogen from a gaseous mixture containing hydrogen, typically an active carbon and/or a zeolite.

- The PSA unit 1 comprises an inlet 2 receiving a feedstock gas at high pressure, typically between 15 and 45 bar, in a pipe 3 leading for example from a catalytic reforming unit and containing at least 60%, advantageously at least 70%, hydrogen. The PSA unit 1 comprises an outlet 4 feeding into a supply pipe 5, more or less at the same pressure as the feedstock gas, supplying high-purity hydrogen to user stations 6 on the site.
- The PSA unit 1 comprises at least one waste gas outlet 7, impoverished in hydrogen, leading, via a pipe 8 incorporating an extraction compressor 9, to a line 10 conveying, on the site, a fuel gas mixture intended to be fed to other user stations, typically burners 11 for

heating active or passive parts of the industrial site and containing at least 30%, and advantageously between 35 and 50%, hydrogen.

Using this arrangement, the waste gas is extracted, at the outlet 7, at a low pressure, of the order of 1.1 to 2 bar, and is compressed, by the compressor 9, to the pressure obtaining in the line 10, typically ranging between 3 and 8 bar.

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According to one aspect of the invention, a pipe 12 incorporating a compressor 13 connects a point of the line 10 upstream of the region of connection of the line 10 to the pipe 8 to the feedstock gas supply pipe 3, the compressor 13 raising the fraction of the stream of fuel gas mixture tapped from the line 10 to the high pressure of the pipe 3 in order to reinject an additional quantity of hydrogen available in the fuel gas mixture into the feedstock gas.

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According to one aspect of the invention, the compressors 9 and 13 are arranged in such a way as to share certain subassemblies, for example a common oil system, a common cooling system, or even a common drive system, as embodied by the line 14 in the figure.

Thus, for preference, the two compressors 9 and 13 are combined into a single machine with one or several stages devoted to each of the compressors, it being possible for said stages to be pistons, impellers, screws.

By thus integrating functionalities of the two compressors it is possible to make economies of scale of the order of 30 to 40% on the investment.

Although the invention has been described in conjunction with some particular embodiments, it is not restricted thereto but can be modified and varied in

ways which will be evident to the person skilled in the art within the scope of the claims that follow.

Thus the injection of part of the stream of fuel gas mixture into the PSA unit 1 via the pipe 12 may be performed separately from the admission of main feedstock gas 3 into the PSA unit 1 if the cycle adopted for the latter so permits (particularly in the case of several cylinders simultaneously in the production phase).

Furthermore, also depending on the cycles of the PSA unit 1, it is possible to inject a fraction of the waste available at the outlet 7 of the PSA unit 1 directly into the network 10, without compression, for example at the start of the depressurization of an adsorber, the waste then being compressed by the compressor when the pressure in the adsorber cylinder decreases.

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Finally, a stream of fuel gas mixture may be tapped from a network operating in parallel with the network 10 receiving the waste from the PSA unit, provided that this parallel network is carrying a gaseous mixture containing at least 30% hydrogen.